Low-Temperature Emission Control to Enable Fuel-Efficient Engine Commercialization

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This presentation does not contain any proprietary, confidential, or otherwise restricted information



NTRO

Acknowledgements

- ORNL Low Temperature Catalysis Team
 - Eleni Kyriakidou*, Andrew Binder, Jae-Soon Choi, James E. Parks











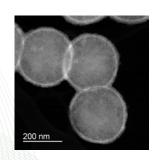
- DOE funding
 - Advanced Combustion Systems
 - Ken Howden, Gurpreet Singh, and Leo Breton



Energy Efficiency & Renewable Energy

VEHICLE TECHNOLOGIES OFFICE

- Access to instrumentation
 - Micrographs and elemental maps captured using instrumentation (FEI Talos F200X S/TEM) provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the **Nuclear Science User Facilities**





Project Overview

Timeline

Year 2 of 3-year program*

Budget

- FY2016: \$400k (Task 1*)
- FY2017: \$400k (Task 1*)

*Task 1: Low Temperature Emission Control

Part of large ORNL project "Enabling Fuel Efficient Engines by Controlling Emissions" (2015 VTO AOP Lab Call)

Partners

- Low Temperature Aftertreatment Sub-Team of US DRIVE Advanced Combustion and Emission Control Tech Team
- Johnson Matthey
- Solvay
- NSF-funded scientists/students
 University of South Carolina
- Karlsruhe Institute of Technology

Barriers

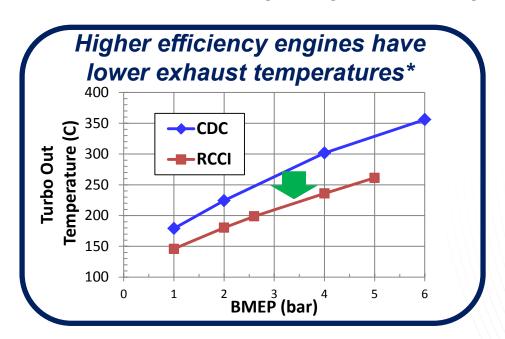
- From DOE Vehicle Technologies
 Multi-Year Program Plan
 - 2.3.1.B: Lack of cost-effective emission control
 - 2.3.1.D: Durability
- Overall, addressing emission compliance barrier to market for advanced fuel-efficient engine technologies

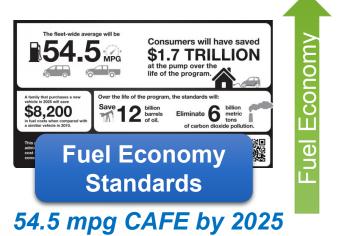


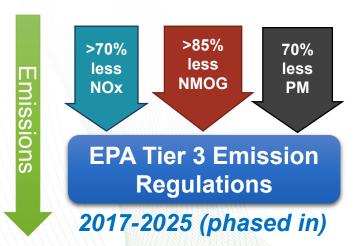
Objectives and Relevance

Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures (<150°C) to meet emission regulations Goal: 90% Conversion at 150°C

- Greater combustion efficiency lowers exhaust temperature
- Catalysis is challenging at low temperatures
- Emissions standards getting more stringent







^{* -} Reactivity Controlled Compression Ignition (RCCI) [a Low Temperature Combustion model vs. Conventional Diesel Combustion (CDC)

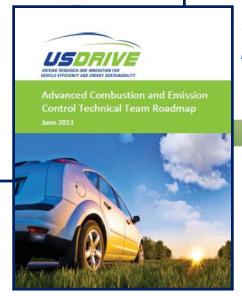


Relevance: Guiding Documents Define Needs



2015 CLEERS Industry Priorities Survey

USDRIVE "The 150°C Challenge"
Workshop Report



USDRIVE ACEC Tech Team Roadmap (2013)

Relevant to all combustion approaches cited in ACEC Tech Team Roadmap

Identified Needs Addressed:

- Lower temperature CO and HC oxidation
- Low temperature NOx reduction
- Cold start emission trapping technologies
 - Especially passive NOx adsorbers
- Reduced PGM
- Better durability
- Promote innovative catalytic solutions via partnering with DOE BES programs

Low Temperature Combustion (LTC)

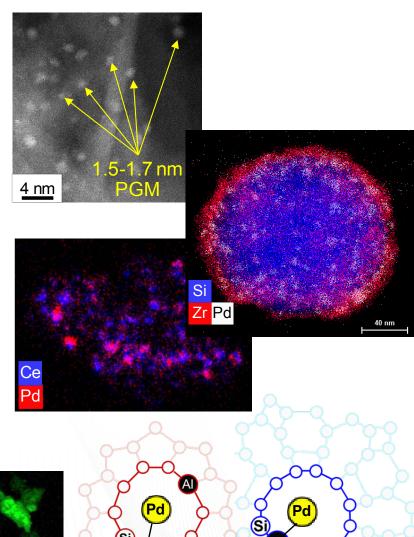
Dilute Gasoline Combustion

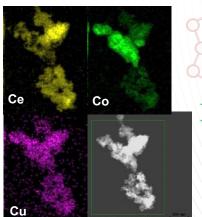
Clean Diesel
Combustion (CDC)

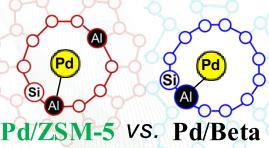


Approach

- Advanced concepts through collaborations
 - Universities and BES-funded scientists
 - Evaluate promising materials w/ ACEC protocols
- Enhance conventional catalysts through support modifications
 - Maximize PGM usage and improve durability
 - Core@shell approaches with metal oxides
 - Targeted deposition PGM on nanoparticles of Ce- and Ce-Zr supported on alumina
- Passive adsorber/trap materials
 - Hold onto emissions until catalysts are active
 - Passive NOx adsorbers
 - Hydrocarbon traps
- Novel materials (high risk)
 - PGM free metal oxides









Approach: employ low temperature protocols to evaluate novel catalysts

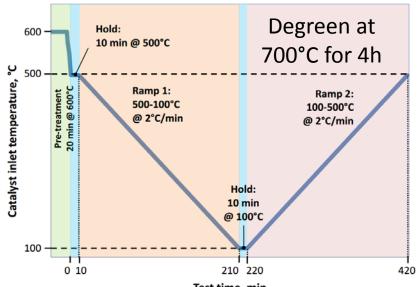
- Protocol finalized in June 2015 by the Low Temperature Aftertreatment Sub-Team of the US DRIVE Advanced Combustion and **Emission Control Team**
- Full file at: www.CLEERS.org

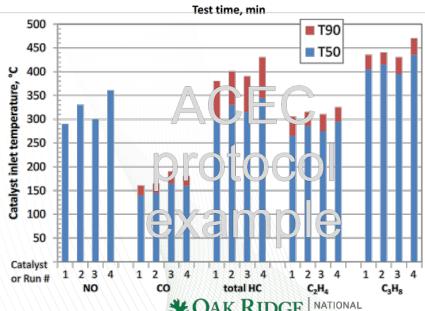
LTC-D: Low Temp. **Combustion Diesel**

Total HC₁: 3000 ppm C_2H_4 : 1667 ppm C_3H_6 : 1000 ppm C_3H_8 : 333 ppm CO: 2000 ppm 100 ppm NO: H_2 : 400 ppm H_2O : CO_2 : O_2 : 12 % Balance N₂

Powder Catalyst Requirements

- Reactor ID 3-13 mm
- Catalyst particle size $\leq 0.25 \text{ mm } (60 \text{ mesh})$
- Catalyst bed L/D ≥ 1
- Space velocity
 - 200-400 L/g-hr
 - For 0.1 g sample, flow 333-666 sccm





^{* -} we employed decane (C₁₀H₂₂) due to bubbler needs

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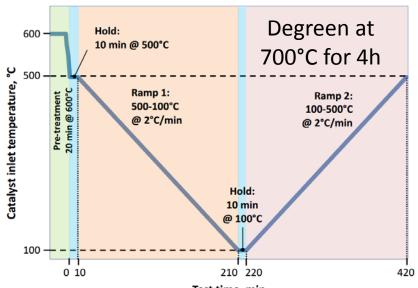
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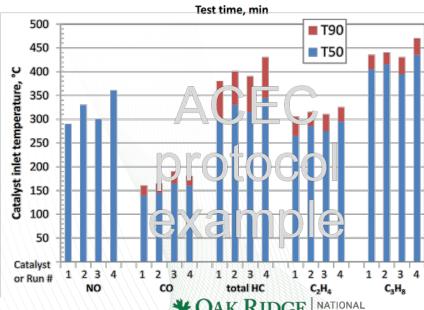
LTC-D: Low Temp. **Combustion Diesel**

Total HC₁: 3000 ppm C_2H_4 : 500 ppm C_3H_6 : 300 ppm C_3H_8 : 100 ppm *C₁₂H₂₆: 2100 ppm CO: 2000 ppm NO: 100 ppm H_2 : 400 ppm H₂O: 6 % CO_2 : O_2 : 12 % Balance N₂

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Collaborations

DOE Basic Energy Sciences Program

Sheng Dai and Ashi Savara (ORNL), Center for Nanophase Material Science (ORNL)

CLEERS

Dissemination of data; presentation at CLEERS workshop

Academia

- University of South Carolina: Professors John Regalbuto, Jochen Lauterbach and Erdem Sasmaz
- Karlsruhe Institute of Technology: Professor Olaf Deutschmann and Andreas Gremminger
- University of Tennessee: Professors Siris Laursen and Sheng Dai

Industry

- **USCAR/USDRIVE ACEC Low Temperature Aftertreatment (LTAT) Sub-Team**
 - low temperature evaluation protocols
- Catalyst and washcoat suppliers
 - **Johnson Matthey:** Industry input from Haiying Chen
 - **Solvay:** alumina-based supports provided for PGM support studies at USC (Barry Southward)

Other DOE-funded FOA Projects

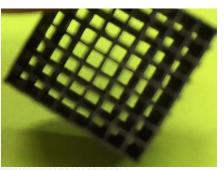
- Ford-led project: Next Generation Three-Way Catalysts for Future, Highly Efficient Gasoline Engines
 - Catalysts being investigated for stoichiometric applications
- UCONN-led project: Metal Oxide Nano-Array Catalysts for Low Temperature Diesel Oxidation



Milestones

- FY16 Milestones: complete
 - Report on evaluation of CCC+PGM emissions control studies including implementation of full ACEC low temperature protocol (9/30/2016).
 - 2016 Annual Merit review
 - 2016 CLEERS Workshop
 - 2016 DOE Annual Report
 - Manuscript in preparation
- FY17 Milestones: on track
 - Develop capability to washcoat novel powder catalysts (9/30/2017).
 - Initial coatings too thick
 - Second effort needed two dips to obtain CCC loading of 1-2 g/in³





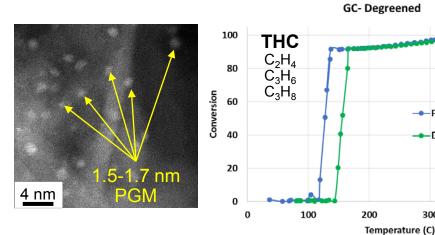
Summary of Technical Accomplishments

- ORNL/USC/Solvay Collaboration PGM/advanced supports
 - Series of Pt:Pd DOCs synthesized at USC (Univ. of South Carolina) on Solvay supports
 - Evaluated and aged at ORNL with ACEC protocols
 - 2% Pt on 80% Al₂O₃ / 20% SiO₂ shows promising results
- Enhance conventional catalysts through support modifications
 - Including Pt on both Ce/Zr nanoparticle approach and SiO₂@ZrO₂ core@shell catalysts greatly enhanced HC activity
 - Although Pt and Pd on same support did not yield benefit, physical mixtures of the two show promise
- Trapping materials
 - Expanded on Ag/zeolite studies to include Pd ion-exchanged materials
 - Pd/ZSM-5 catalyst shown to have good HC and NOx trapping ability
 - Combining best trap and best DOC showed excellent low temperature behavior and sulfur tolerance
- PGM-free mixed metal oxides
 - Addition of Mn to CCC-based mixed metal oxide significantly improved high space velocity CO activity and sulfur tolerance



University of South Carolina (USC) and Solvay collaboration yielding promising results for stable PGM catalysts

- Prof. Regalbuto (USC) has been leading research on Strong Electrostatic Adsorption (SEA) of PGM on standard supports
 - Superb initial PGM dispersion
 - Durability has been an issue
- Solvay collaboration started
 - A leader in stable supports
 - Provided 7 supports
 - 70-100% AI, 0-30% Si, 0-4% La
- USC synthesis of Pt:Pd DOCs
 - Target PGM total: 2 wt%
 - Pt:Pd 1:0, 3:1, 1:1, 1:3, 0:1
- Very promising results obtained with ACEC protocols
 - 2% Pt on 80% Al₂O₃ / 20% SiO₂



Fresh

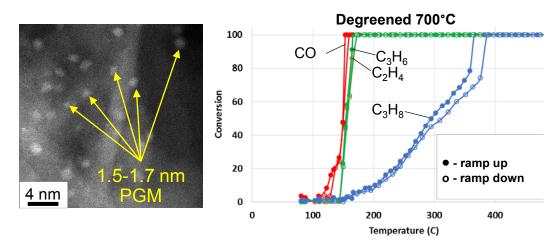
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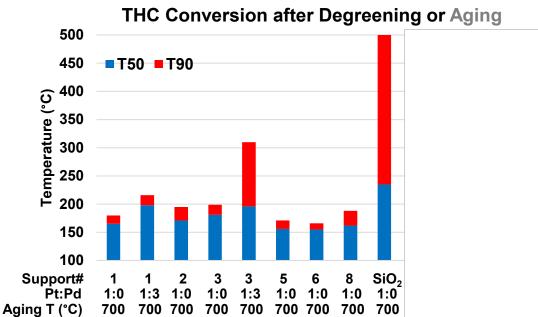
Degreened@700C

400

University of South Carolina (USC) and Solvay collaboration yielding promising results for stable PGM catalysts

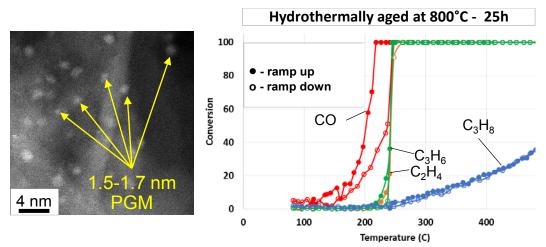
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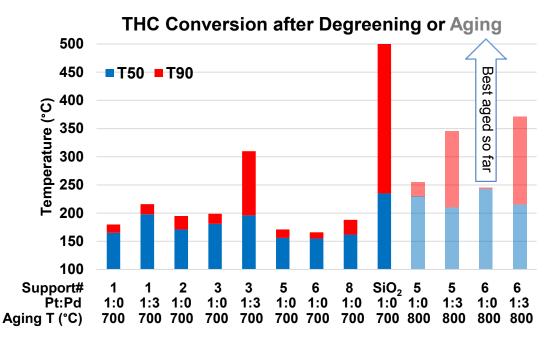




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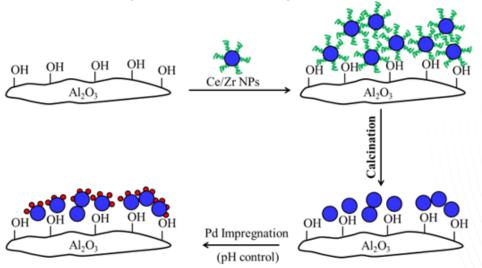
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- Very promising results obtained with ACEC protocols
 - 2% Pt on 80% Al₂O₃ / 20% SiO₂
 - More samples to age

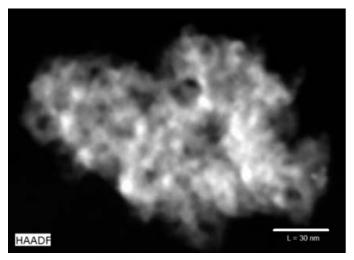


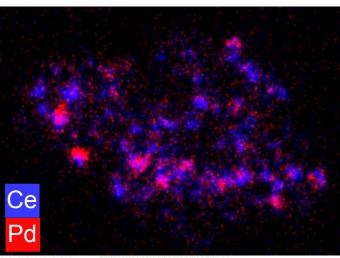


Targeted PGM deposition on nanoparticles of CeO₂ and CeO₂-ZrO₂ to improve durability and activity

- Starting with Ce or CeZr nanoparticles,
 ~5 nm, and anchor them to high surface area supports
 - In this instance Al₂O₃, but SiO₂ also possible
- Target Pd or Pt deposition on preferred supported metal oxide
 - nano-particles of PGM on nano-particles of Ce-Zr
 - controlling pH enables targeted deposition





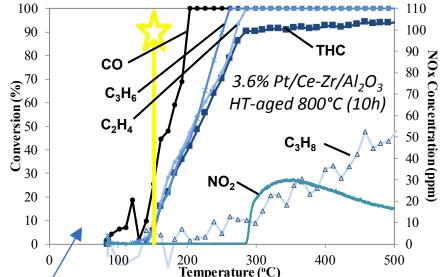


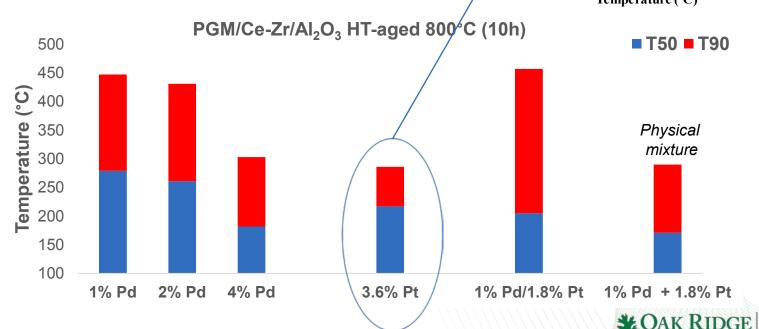


Pd NPs

PGM/Ce-Zr/Al₂O₃ catalysts show promise, but best catalysts require high PGM content

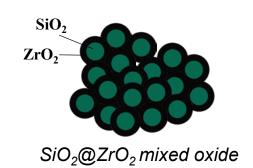
- Some promising results observed
 - Especially for Pt containing catalysts
 - HT-aged at 800°C data shown
- However, meeting 150°C target still challenging, especially C₃H₈
 - Interestingly, this material has better performance under S-GDI conditions*

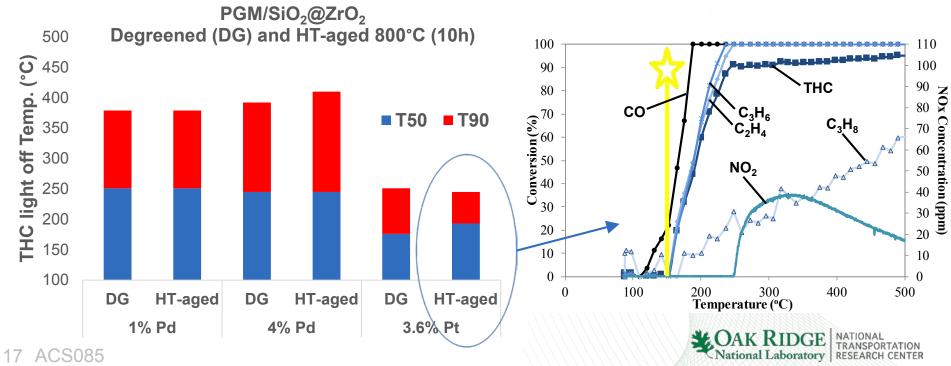




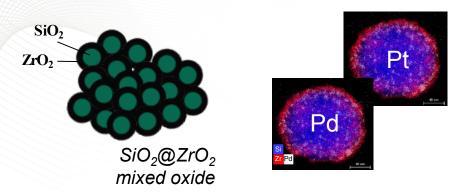
Novel synthesis technique successfully creates ZrO₂ shell around SiO₂ core

- Able to synthesize a complete ZrO₂ shell around SiO₂ core using novel technique
 - PGM/SiO₂@ZrO₂
 - PGM deposition solely on outer ZrO₂ shell
- While employing ACEC low temperature protocols improved activity shown with this technique
- Durable after aging at 800°C for 10h

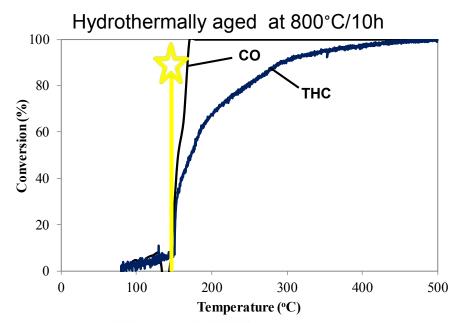


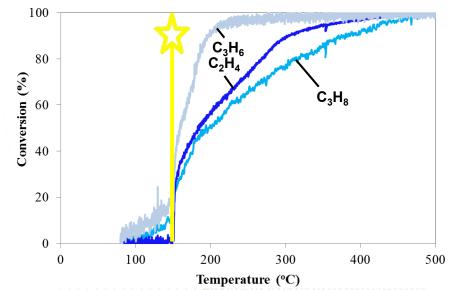


Core-shell concept has led to excellent activity in Pd + Pt physical mixture after HT-aging at 800°C

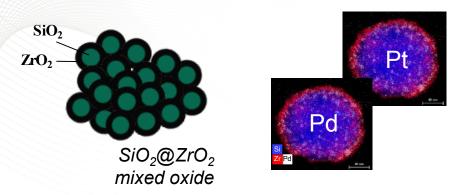


- PGM supported on a shell of ZrO₂ around a core of SiO₂ (SiO₂@ZrO₂)
- Exceptional low temperature activity observed with Pt+Pd physical mixture
 - Bed loading: 1.8% Pt and 1.0% Pd

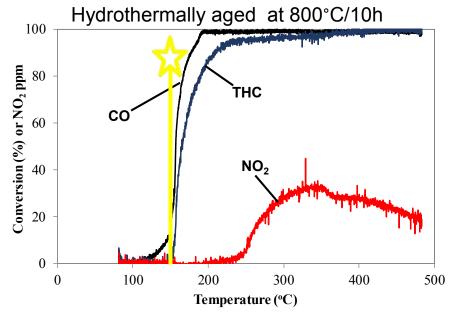


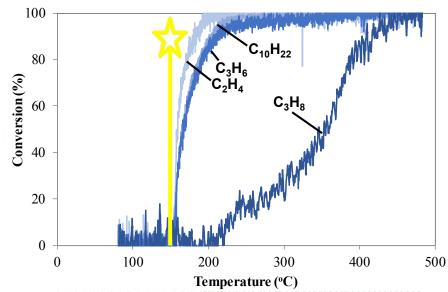


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- Exceptional low temperature activity observed with Pt+Pd physical mixture
 - Bed loading: 1.8% Pt and 1.0% Pd
- Also, active with liquid hydrocarbon LTC-D protocol using decane (C₁₀H₂₂)





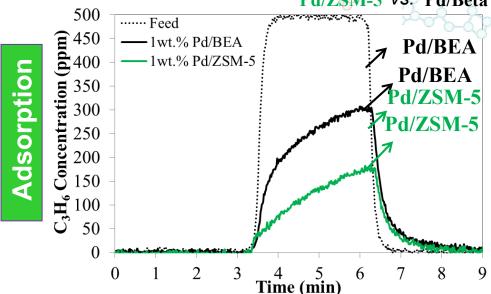
Pd/ZSM-5 catalyst has good HC and NOx trapping ability*

Pd/ZSM-5 VS. Pd/Beta

- ❖ C₃H₆ adsorption is sensitive to the type of metal.
- Arr Pd/ZSM-5 shows the best C_3H_6/NOx trapping ability.

Adsorption Conditions:

C₃H₆: 167 ppm, 200 ppm NO, 10% O₂, 5% H₂O, balance Ar, Total Flow: 600 sccm, SV: 90,000 h⁻¹



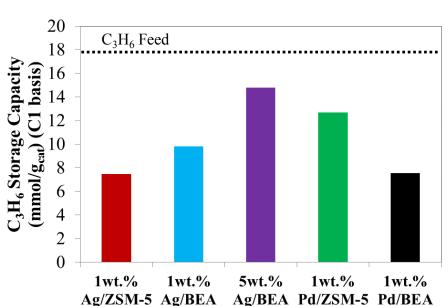
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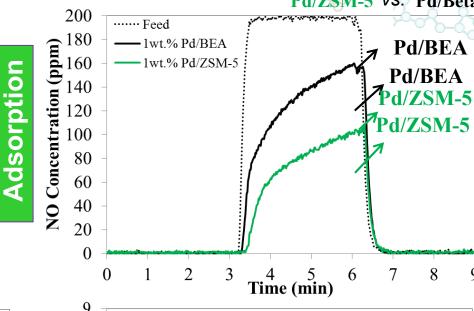
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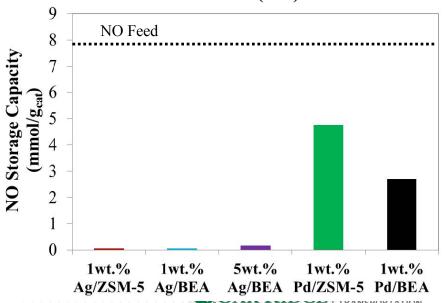
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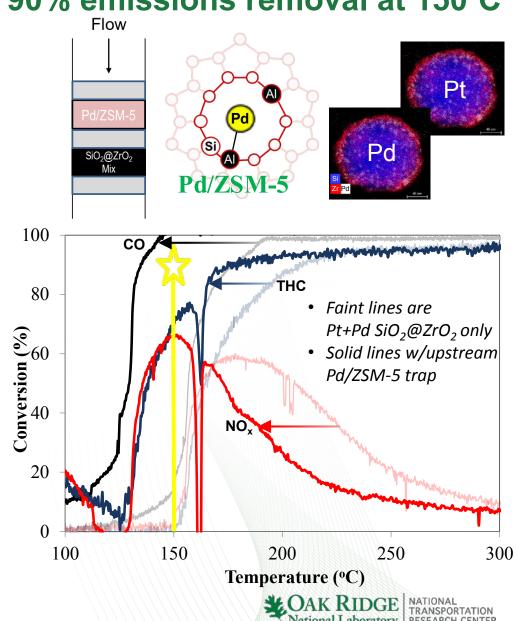




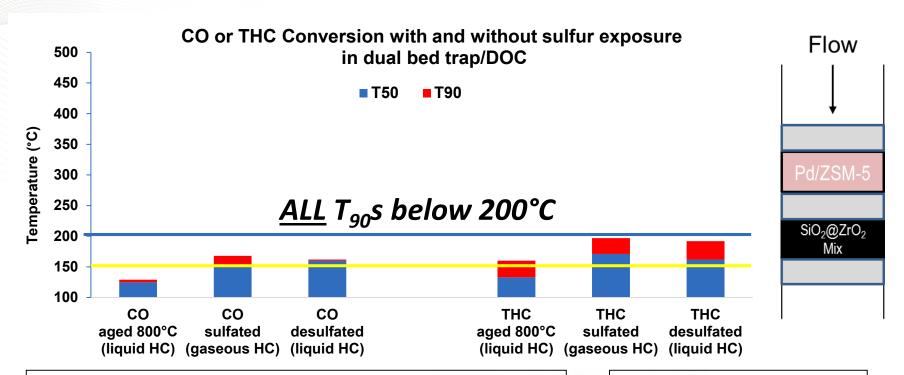


Combining the HC/NO trap material and the best oxidation catalyst shows pathway to 90% emissions removal at 150°C

- Experimental conditions
 - Dual bed exposure
 - 1st bed Trap: Pd/ZSM-5
 - 2nd bed Pt+Pd SiO₂@ZrO₂ core-shell
 - 1.8%Pt + 0.5%Pd
 - HT-aged at 800°C (2h)
 - Reactor at 80°C with liquid LTC-D flowing in bypass (including C₁₀H₂₂)
 - Switch flows from bypass to dual bed and immediately begin heating
 - at 5°C/min to 500°C
- Trapping of both NOx and HC results in very low CO light off
- Good NO and HC removal below 150°C, followed by release at 160°C
 - Good conversion observed of HC after release



Employing ACEC sulfur protocol in dual bed trap/DOC illustrates excellent tolerance and activity



Sulfation protocol

- 5 ppm SO₂ at 300°C for 5 h in full simulated exhaust
- Sulfation and sulfur evaluation performed with gaseous HCs
 - Initial and desulfated evaluation performed with liquid hydrocarbon protocol

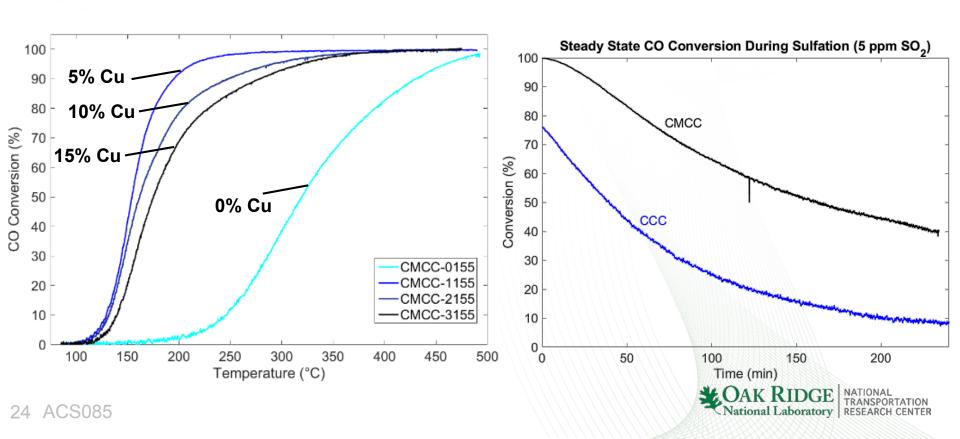
Desulfation procedure

- Lean-rich cycling at 500°C for 30 minutes
- Desulfated evaluation starting at 80C with liquid hydrocarbons



Addition of Mn to CCC formulation improved reactivity of sample under LTC-D conditions; optimal Cu loading found

- Manganese (1%) added to formulation based on interesting low temperature SCR studies
 - Unfortunately no increase in NO to NO₂ oxidation observed (not shown)
- Varying the copper level from 0 to 15% shows that the 1:1:5:5 (Cu:Mn:Co:Ce) ratio illustrates optimal performance



Remaining Challenges

Future Directions

Support modifications for enhanced PGM activity

PGM content should be as small as possible especially for Pt-containing catalysts

Pt-Pd interactions have been shown to have significant advantages, but whys is this only observed in physical mixtures here?

USC/Solvay collaboration shows excellent initial activity but needs improved durability

Trapping Materials

Pd/zeolites show excellent effectiveness. but characterization illustrates improved ion-exchanging is necessary

BEA and ZSM-5 zeolites not expected to be hydrothermally stable above 750°C

PGM-free mixed metal oxides

Unclear if significant role exists for CMCC in combined/dual-bed system

Develop understanding of Pt loading impact on reactivity and durability to enable thrifting of PGM content

Perform extensive bi-metallic materials characterization of the fresh and aged samples to better understand PGM state

Complete aging study on existing catalysts and then explore introduction of optimized metal oxide overlayer

Improve ion-exchange by systematically modifying procedure followed by characterization

Find failure point of materials plus ones w/ improved ion-exchange; explore CHA; also MECA-member provided materials

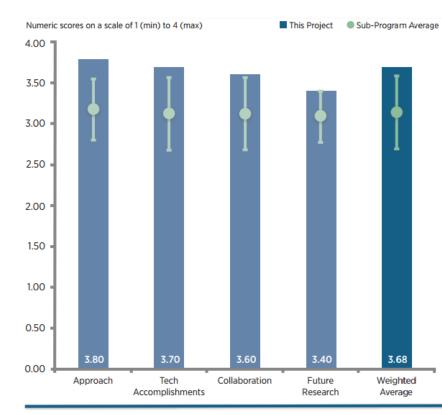
Evaluate impact of addition to the dual bed in physical mixture and washcoated with PGM-based oxidation catalysts

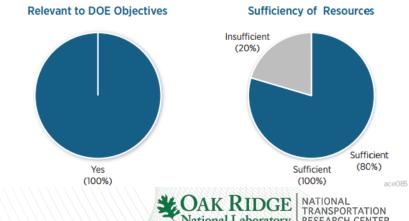
Any proposed future work is subject to change based on funding levels



Responses to 2015 Reviewers (5); overall score = 3.68/4.00

- Approach (3.8/4.0): methods used in analyzing the catalytic materials in the project as excellent... consider
 HC chains and aromatics ... how does S alter the activity of the catalysts
- Technical Accomplishments (3.7/4.0): very interesting and potentially useful ... need to understand why PGM inclusion improves S tolerance with CCC ... commend the project team for considering both thermal aging and S poisoning ... CO₂ needed in trap evaluations ... Rh should be considered for evaluations
- Collaborations (3.6/4.0): interaction with the automotive OEMs and catalyst formulators increases the value of the research ... OEM would also be a helpful partner
- Future plans (3.4/4.0): future work is appropriate and in line with funding.... sound technical path forward ... hard to tell if trapping will receive the attention it deserves ... effect of sulfur should be the top priority.... Include other HCs
- Relevance (100%): by enabling the use of more efficient combustion, these systems support the move to improving overall fuel economy... low-temperature catalysis is the key barrier to high efficiency combustion strategies
- Resources (20% Insufficient): more resources necessary to meet project and program goals, especially for the NH₃ SCR





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Responsive Actions

- 1. Following LTC-D protocol for liquids this year...aromatics included in new trapping protocol (backup slides)
- 2. S included in all facets this year
- 1. Further research performed in this area for publication, but not major focus
- 2. Examined CO₂ impact in traps; minimal observed, thus removed for C-balance
- 3. Rh catalysts synthesized, but results are not promising to date
- 1. Efforts to coordinate and collaborate with OEMs are ongoing
- 1. Efforts this year give a good balance between trapping and oxidation
- 2. Sulfur included; Pd-traps high tolerance
- 3. Full HC mixture included this year; more in backup slides
- NH₃-SCR evaluation not currently planned; NOx efforts currently focused on adsorber/traps

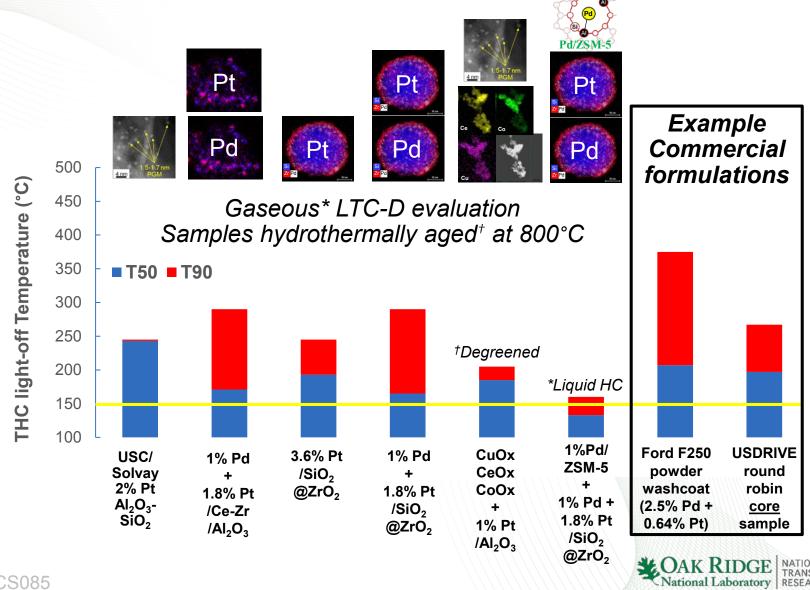
Summary

- **Relevance:** Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures (<150°C) to meet emission regulations
- Approach: employ low temperature protocols to evaluate novel catalysts
- Collaborations: Wide-ranging collaboration with industry, academia, & national labs maximizes breadth of study, guides research from other funding sources
- Technical Accomplishments:
 - Series of Pt:Pd DOCs synthesized at USC on Solvay supports evaluated & aged at ORNL
 - Physical mixtures of Pt and Pd SiO₂@ZrO₂ supports show excellent activity with greatly enhanced HC activity
 - Expanded on Ag/zeolite HC/NO trapping studies to include Pd ion-exchanged zeolites
 - Pd/ZSM-5 catalyst shown to have good HC and NOx trapping ability
 - Combining best trap and best DOC showed excellent low temperature behavior and sulfur tolerance
 - Addition of Mn to CCC-based mixed metal oxide significantly improved high space velocity CO activity and sulfur tolerance
- Future Work: continued efforts on thrifting optimizing PGM usage, improved durability, and characterization to understand bi-metallic PGM interactions; have internal (ORNL) funding to explore potential commercialization on candidates



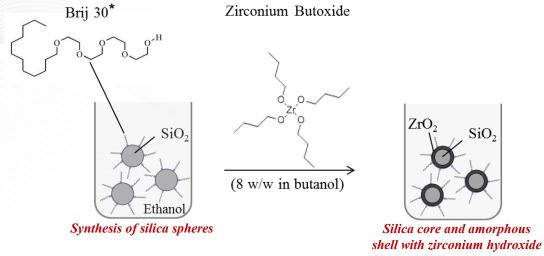
Technical Backup Slides

New formulations compare favorably to modern commercial DOCs after HT aging at 800°C



Experiment Detail: Synthesis of SiO₂@ZrO₂ core@shell

Oxide Support

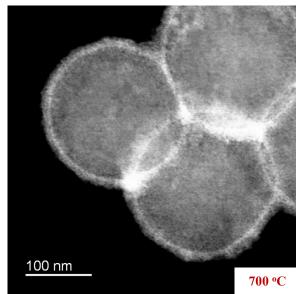


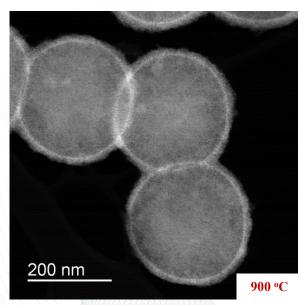
Material	Surface Area (m²/g)	ZrO ₂ SiO ₂ Aging for 3 days oc
ZrO ₂	97	ZrO ₂ SiO ₂ Aging from a single sin
ZrO ₂ -SiO ₂	153	Ø ∠Cale
SiO ₂ @ZrO ₂	210	\rightarrow 0 \circ

Silica core and zirconium oxide shell after calcination at 700 °C

- SiO₂ is located in the core (Si: 14 amu) and ZrO₂ in the shell (Zr: 40 amu).
- The ZrO₂ shell seems to be porous.
- Growth of SiO₂@ZrO₂ spheres. Shell is maintained. Diameter at: 700 °C: ~220 nm

900 °C: ~250 nm







LTAT Protocol - Storage

Table 2 - Step 1 of protocol: Pre-treatment

PRE-TREATMENT — CDC, LTC-D, LTC-G, L-GDI										
Step No.	Temperature	Exhaust make-up (balance N ₂)* Bypa								
LTP-2-1P	Pretreat 20 min @ 600°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	Off	
LTP-2-2P	Cool 600°C to 100°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	Off	
LTP-2-3P	Hold 5 min @ 100°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	Off	

PRE-TREATMENT — S-GDI										
Step No.	Temperature		Bypass							
LTP-2-1PS	Pretreat 20 min @ 600°C	-	-	-	-	[O ₂]	[H ₂ O]	[CO ₂]	Off	
LTP-2-2PS	Cool 600°C to 350°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	Off	
LTP-2-3PS	Reduce 5 min @ 350°C	-	3% CO	1% H ₂	-	-	[H ₂ O]	[CO ₂]	Off	
LTP-2-4PS	Cool 350°C to 100°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	Off	
LTP-2-5PS	Hold 5 min @ 100°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	Off	

Bracketed concentration values are combustion-mode dependent and found in Table 1

Table 3 -Step 2 of protocol: Storage

STORAGE — all modes										
Step No.	Temperature	Exhaust make-up (balance N ₂)* Time Bypass							Bypass	
LTP-2-3S	Hold 100°C	[HC]	[CO]	[H ₂]	[NO]	[O ₂]	[H ₂ O]	[CO ₂]	-**	On
LTP-2-4S	Hold 100°C for 30 min	[HC]	[CO]	$[H_2]$	[NO]	[O ₂]	[H ₂ O]	[CO ₂]	30 min	Off

Bracketed concentration values are combustion-mode dependent and found in Table 1

Table 4 - Step 3 of protocol: Release (and/or conversion)

	NOx RELEASE — all modes										
Step No.	Temperature	Exhaust make-up (balance N₂)* Time Bypass								Bypass	
LTP-2-5RN	Ramp 20°C/min to 600°C	-	-	-	[NO]	[O ₂]	[H ₂ O]	[CO ₂]	26 min	Off	
	HC RELEASE — CDC, LTC-D, LTC-G, L-GDI										
Step No.	Temperature		Exha	ust ma	ke-up	(balan	ce N ₂)+		Time	Bypass	
LTP-2-5RH	Ramp 20°C/min to 600°C	-	-	-	[NO]	[O ₂]	[H ₂ O]	[CO ₂]	26 min	Off	
	HC RELEASE— S-GDI										
Step No.	Temperature		Exha	ust ma	ke-up	(balan	ce N ₂)+		Time	Bypass	
LTP-2-5RHS	Ramp 20°C/min to 600°C	-	-	-	-	-	[H ₂ O]	[CO ₂]	26 min	Off	

^{*} Bracketed concentration values are combustion-mode dependent and found in Table 1

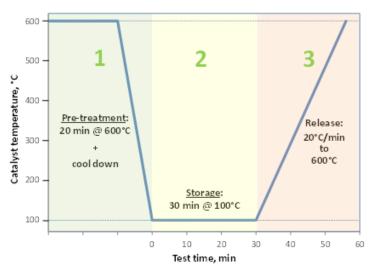


Figure 3 - Storage protocol temperature control

Table 5 - Catalyst de-greening parameters

S-GDI, L-GDI, LTC-G										
Step No.	Mode	Condition	Exhaust make-up (balance N ₂)							
			[O ₂]	[CO ₂]	[H ₂ O]					
LTP-1DG-G	Neutral	700°C/4 hours	-	10%	10%					
		CDC, LTC-D								
Step No.	Mode	Condition	Exhaust	make-up (l	oalance N ₂)					
			[O ₂]	[CO ₂]	[H ₂ O]					
LTP-1DG-D	Lean	700°C/4 hours	10%	5%	5%					

^{**} For inlet characterization; dependent on time required to stabilize inlet concentrations

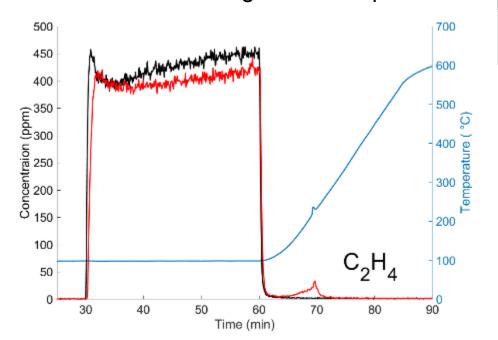
Employing ACEC storage protocol in future trapping experiments with liquid hydrocarbons

ACEC Low-Temperature Storage Catalyst Test Protocol (in draft phase) calls for 30 minutes of storage at 100 °C with multiple liquid hydrocarbon species as well as standard exhaust gasses (CO, NO, H_{2, etc...})

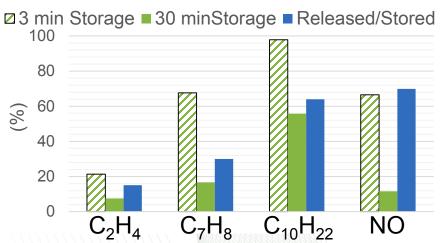
Pd/ZSM-5 stores a considerable amount of NO, toluene and decane with a peak

release centered around 210 °C

Pd/ZSM-5 Storage and Ramp



	C ₂ H ₄	C ₇ H ₈	C ₁₀ H ₁₂	NO
Total Stored (mg/g _{cat})	2.11	4.43	21.32	0.78
3 min storage (mg/g _{cat})	0.52	0.95	2.04	0.45



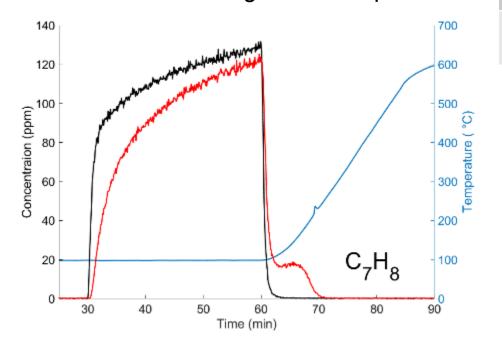
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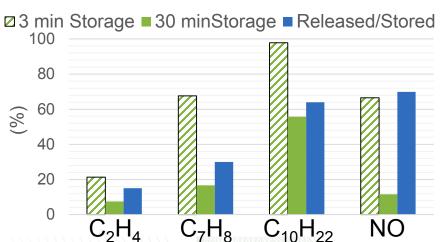
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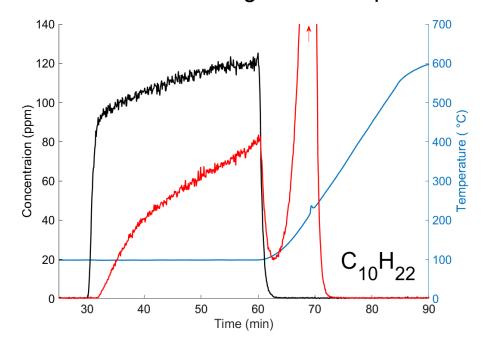
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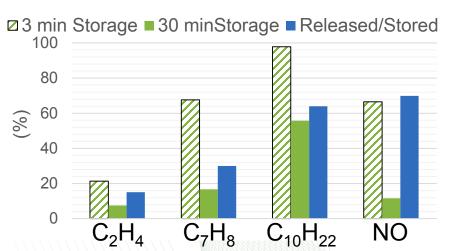
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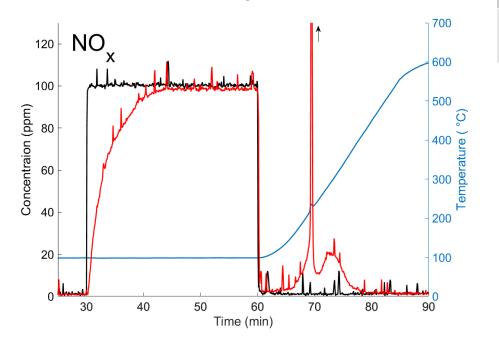
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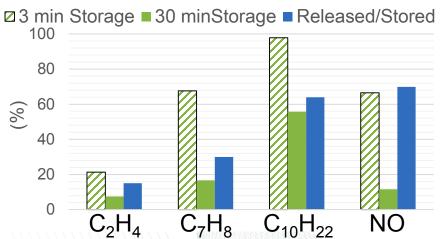
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CCC by Glycine-Nitrate "Combustion" Synthesis Shows Increased Surface Area and Performance for Lean Exhaust



- CCC was synthesized by glycine-nitrate process (metal nitrates mixed with glycine and brought to auto-combustion temperature). This process is more easily scalable than coprecipitation and results in a fine powder with a nearly 10 fold increase in apparent volume at 100 mg, suggesting greatly increased surface area.
- Resulting degreened CCC powder shows lower T₉₀
 temperatures for CO conversion and greatly increased HC
 performance during LTC-D exhaust testing. This is likely a
 result of the greatly enhanced surface area of the catalyst.

